

CORRECTED VERSION

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- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: THERMOPLASTIC FILM FOR PACKAGING

(57) Abstract: A thermoplastic shrinkable film consisting of two or more layers, including, at least, (a) a layer of a polyolefin, (b) a layer of a blend of a polyolefin and an ionomer is disclosed. Optionally, the film contains (c) a further layer of a polyolefin, in which case layer (b) is positioned between layers (a) and (c). Films according to this invention demonstrate omnidirectional tearability, good clarity and strength and are cost competitive with other films on the market.

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TITLE

Thermoplastic Film for Packaging

BACKGROUND OF THE INVENTION

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The present invention relates to thermoplastic, shrinkable film intended for packaging purposes, more particularly for bundling unit packs of individual objects, such as tinned goods, cans, bottles or the like. This film is particularly suitable for packaging PET bottles.

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Bundling is a method which consists of surrounding all of the objects to be packaged with a shrinkable thermoplastic resin film which can be welded back onto itself, so as to form a sleeve around the objects. The package is then shrunk by, for example, passing it through an oven at a temperature that enables the thermoplastic resin constituting the film to soften, thereby relieving internal stresses. Upon leaving the oven, rapid cooling ensures that the film closes tightly around the objects contained therein. This yields a bundle in which the thermoplastic film performs the function of a skin in close contact with the surface of the packaged objects.

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Various thermoplastic shrinkable packaging films are known. Representative are those described in EP 0 537 080 B1, GB 2 290 500 A and US 5,630,307.

EP 0 537 080 B1 describes a film having at least two layers, one being a polyolefin, the other being an ionomer, which is blow co-extruded under particular conditions such that the film has a tear preference perpendicular to the direction of extrusion of the film.

GB 2 290 500 A discloses films based upon a substrate of polyolefin and ionomer. One such film is a three-layer film having a central layer of ionomer and two outer layers of polyethylene. A second film mentioned is a monolayer of a blend of polyethylene and ionomer. US 5,630,307, as well, discloses monolayer films made from blends of ionomer and polyethylene.

Although the films described in these documents function well in many circumstances, each has certain drawbacks. The monolayer films tend to have poor clarity and lack strength needed for bundling heavier objects. The multilayer film described in GB 2 290 500 requires, in practice, a relatively thin layer of ionomer, which is difficult to produce on standard industry equipment. The multilayer film of EP 0 537 080 B, as previously mentioned, tears preferably perpendicular to the direction of extrusion. In certain cases, however, it is preferable to have omnidirectional tearability.

SUMMARY OF THE INVENTION

The thermoplastic shrinkable film of the present invention has omnidirectional tearability, good clarity and strength and is cost competitive with other films on the market. It consists of two or more layers, including, at least, (a) a layer of a polyolefin, (b) a layer of a blend of a polyolefin and an ionomer. Optionally, the film of the present invention contains (c) a further layer of a polyolefin. In the case layer (c) is present, layer (b) will be positioned between layers (a) and (c).

DETAILED DESCRIPTION OF THE INVENTION

Suitable polyolefins to be used in layers (a), (b) and (c) are known in the art. They may be homopolymers of α -olefins or copolymers of such olefins with one or more monomers, as well as mixtures thereof.

The α -olefin copolymer is a copolymer of α -olefins of the formula $R'-CH=CH_2$, wherein R' is hydrogen or an alkyl radical having 1 to 8 carbon atoms, with at least one further monoethylenically unsaturated monomers, such as aliphatic or aromatic monomers. Suitable such monoethylenically unsaturated monomers include vinyl acetate, styrene and (meth)acrylic derivatives. This other monomer can represent up to 20% by weight of the olefinic copolymer, preferably 1 to 10% by weight.

- Suitable polyolefins for use in the invention include polyethylene, polypropylene, copolymers of ethylene and propylene, ethylene-vinyl acetate copolymers, copolymers of ethylene and acrylic derivatives, terpolymers based on olefin, methyl acrylate and ethyl acrylate, as well as mixtures of these. Preferred polyolefins are low density polyethylenes (LDPEs) and blends of LDPEs and high density polyethylenes (HDPEs), in a weight ratio of LDPE/HDPE in the range of 95/5 to 50/50.
- 10 Ionomers are known in the art. They are copolymers of ethylene and an α,β -unsaturated C₃-C₈ carboxylic acid, optionally containing at least one softening comonomer that is copolymerizable with ethylene. Acrylic and methacrylic acids are preferred acid comonomers. The softening comonomer can be an alkyl acrylate selected from the group consisting of n-propyl-, n-butyl, 15 n-octyl, 2-ethylhexyl-, and 2-methoxyethyl-acrylates. The preferred alkyl acrylates are n-butyl-, 2-ethylhexyl-, and 2-methoxyethyl-acrylates. The softening comonomer can also be an alkyl vinyl ether selected from the group consisting of n-butyl, n-hexyl, 2-ethylhexyl-, and 2-methoxyethyl-vinyl ether. The preferred alkyl vinyl ethers are n-butyl vinyl ether and n-hexyl vinyl ether. The copolymer is about 10 to 100% neutralized with metal ions selected from groups Ia, Ib, IIa, 20 IIIa, IVa, VIb, and VIII of the Periodic Table of Elements such as sodium, potassium, zinc, calcium, magnesium, lithium, aluminum, nickel, and chromium. Typically, neutralization will be from 10-70%. Preferably the copolymer has from about 35 to about 70% of the carboxylic acid groups ionized by neutralization with metal ions selected from the group consisting of sodium, potassium, zinc, 25 calcium, and magnesium. Ionomers and their methods of manufacture are described in US Patent No. 3,264,272. Suitable ionomers for use in the present invention are available from the DuPont Company, under the trademark SURLYN®.

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The blend used to form layer (b) of the present invention will typically contain a weight ratio of ionomer/polyolefin in the range of 5/95 to 60/40, more preferably 10/90 to 30/70.

- 5 The total thickness of the film according to the present invention will typically be in the range of from 20 to 150 μm , preferably from 30 to 70 μm . The thickness of layers (a) and (c) will range, individually, from 1 to 30 μm , preferably from 3 to 10 μm . The thickness of layer (b) will range from 15 to 140 μm , preferably from 25 to 50 μm . A preferred embodiment of the present invention contains layers (a),
10 (b) and (c). These constructions give the film particularly good clarity.

- 'Omni-directional tearability' means the film of the present invention can be torn by an end-user (e.g. purchaser of packaged bottled water) with relative ease in both the film's machine direction (MD) and transverse direction (TD). Tearability
15 can be measured by the Elmendorf method, which is known in the art. Films of the present invention will have an Elmendorf tear strength in both the MD and TD ranging from 5 to 40 N/mm thickness of film (0.5 to 4 cN/ μm), preferably from 10 to 20 N/mm (1 to 2 cN/ μm).

- 20 The films of the present invention will also preferably demonstrate 'straight line' or near 'straight line' tear in the MD and TD. Straight line tear can be measured as follows:

- Two 50 mm by 200 mm strips of sample films are prepared. In the first sample,
25 the 200 mm length side runs in the MD; in the second sample, the 200 mm length side runs in the TD. A 30 mm cut is made in the center of one of the 50 mm ends of each sample, dividing the end into flaps. Each flap is placed in a jaw of an Instron or Zwick tensile testing machine. The jaws pull apart at a desired speed (e.g. 300 mm/min), thereby tearing an extension of the cut. Preferably, the tear
30 will proceed through the middle of the strip, rather than off to one side.

The polyolefin(s) and ionomer are co-extruded under particular conditions that yield the films according to the present invention. Upon discharge from the die, the film is cooled on a cylinder that is rotating at a speed higher than that of the film discharge rate. This gives the film longitudinal orientation. At the outlet of the flat die, it is also possible to give the film flat bi-axial stretching, using to known techniques.

The conditions under which blown co-extrusion is carried out are as follows. Extruder temperature for the ionomer is in the range of 170 to 220°C, preferably 180 to 200°C. Extruder temperature for the polyolefin is in the range of 160 to 240°C, preferably 180 to 220°C. The temperature of the extrusion die is in the range of 180 to 220°C, preferably 190 to 210°C. The blow-up ratio is in the range of 2 to 5, preferably 2.5 to 3. The blow-up ratio is defined as bubble diameter/die head diameter.

The winding speed is in the range of 5 to 60 m/min, preferably 20 to 30. The extrusion gap is in the range of 0.5 to 3 mm, preferably 1 to 2.

The film of the present invention may contain additional features to make it particularly suitable for packaging applications. One such feature is a tab formed in the film to facilitate initiation of a tear. One such type of tab is described in EP 0 537 079 B1.

Example

A three-layer film having a total thickness of 60 μm is formed as follows:

<u>Material</u>	<u>Source</u>
LDPE.	LUPOLENE 3020 available from BASF
Ionomer.	SURLYN 1601 available from DuPont

Layer (a): LDPE, 10 μm thickness;

Layer (b): 85% LDPE/15% by weight ionomer blend, 40 μ m thickness;

Layer (c): LDPE, 10 μ m thickness

5 The ionomer extruder is maintained at a temperature of 190°C and the LDPE extruder at a temperature of 200°C. The extrusion die temperature is 200°C. The extrusion die gap is set at 1.5 mm. The blow-up ratio is 2.8 and winding speed of the co-extruded film is 30 m/min.

10 Under conventional bundling conditions, a variety of objects such as bottled mineral water are packaged using this film. After initiating a tear in the desired direction, it is possible to continue the tear in that direction without exercising any particular force. Before the tear is initiated, the film maintains all of its shrink and tear resistance properties necessary during the various handling of the bundle.

CLAIMS:

1. A multilayer thermoplastic film adapted for packaging comprising
 - 5 (a) a layer of a polyolefin and
 - (b) a layer of a blend of a polyolefin and an ionomerand demonstrating omni-directional tearability.
- 10 2. A film according to claim 1 further comprising
 - (c) a further layer of a polyolefin, wherein layer (b) is positioned between layers
 - (a) and (c).
- 15 3. A film according to claim 1 or 2, wherein the polyolefin is polyethylene.
4. A film according to claim 3 wherein the polyolefin is low density polyethylene.
5. A film according to any one of claims 1 to 3 wherein the ionomer is a
 - 20 copolymer of ethylene and an α,β -unsaturated C₃-C₈ carboxylic acid,
 - neutralized with metal ions selected from groups Ia, Ib, IIa, IIIa, IVa, VIb,
 - and VIII of the Periodic Table of Elements.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/04046

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B32B 27/08, 27/32

US CL :428/515, 516, 523

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/515, 516, 523

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
None

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2,290,500 A (FAYARD ET RAVEL SA) 03 January 1996, see entire document.	1-4
Y	EP 0,537,080 A (DU PONT DE NEMOURS INTERNATIONAL S.A.) 14 April 1993, see entire document.	1-4
A	US 5,630,307 A (CATHALA) 20 May 1997, see entire document.	1-4

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

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X

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Date of the actual completion of the international search

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Date of mailing of the international search report

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INTERNATI NAL SEARCH REPORT

International application No.

PCT/US99/04046

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☐

No protest accompanied the payment of additional search fees.